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THE TWO-CENTER EXPANSION FOR THE POWERS OF THE DISTANCE BETWEEN TWO POINTS*

by

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ABSTRACT

The powers r^n of the distance between two points specified by spherical polar coordinates relating to two different origins, or of the modulus of the sum of three vectors, are expanded in spherical harmonics of the angles. The radial factors satisfy simple partial differential equations, and can be expressed in terms of Appell functions F_4 and Wigner or Gaunt's coefficients. In the overlap region first discussed by Buehler and Hirschfelder the expressions are valid for integer values of $n \geq -1$, but in the other regions for arbitrary n. For high orders of the harmonics individually large terms in the overlap region may have small resulting sums; as a consequence the two-center expansion is of limited usefulness for the evaluation of molecular integrals.

Expansions are also derived for the 3-dimensional delta function within the overlap region, and for arbitrary functions $f(r)$, valid outside that region.

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THE TWO-CENTER EXPANSION FOR THE POWERS OF THE

DISTANCE BETWEEN TWO POINTS

1. Introduction

The inverse distance between two points Q_1 and Q_2 specified by the polar coordinates $(r_1, \vartheta_1, \varphi_1)$ and $(r_2, \vartheta_2, \varphi_2)$ with respect to a common origin O is given by the well-known Laplace expansion in powers of $r_< / r_>$ and in terms of Legendre polynomials of the mutual direction cosine $(\cos \vartheta_{12})$. For powers other than the inverse first analogous expansions exist either in powers of $r_< / r_>$ or in $P_\ell(\cos \vartheta_{12})$; in the former case the angular dependence is given by Gegenbauer polynomials of $(\cos \vartheta_{12})$[1]; in the latter case the writer has shown in two recent papers that the radial dependence can be expressed by means of Gauss' hypergeometric function[2]

$$F(\alpha, \beta; \gamma; z) = \sum \frac{(\alpha)_w (\beta)_w}{(\gamma)_w \, w!} z^w \quad ; \tag{1a}$$

$$(\alpha)_w = (\alpha; w) = \alpha(\alpha+1)\cdots(\alpha+w-1) = \Gamma(\alpha+w)/\Gamma(\alpha) \quad . \tag{1b}$$

In many physical problems it is more convenient to express the positions of Q_1 and Q_2 in spherical polars about two different origins O_1 and O_2 in such a way that the polar axes and the planes defining $\varphi = 0$ are kept parallel. If the coordinates of O_2 with respect to O_1 are given by $(r_3 = a, \vartheta_3, \varphi_3)$, expansions for the inverse distance in terms of spherical harmonics of the angles have

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[1] L. Gegenbauer, Wiener Sitzungsberichte, 70, 6, 434 (1874), 75, 891 (1877).

[2] R. A. Sack, University of Wisconsin, TCI Reports, Nos. 20 and 24, referred to as I and II respectively.

been given by Carlson and Rushbrooke, by Rose and by Buehler and Hirschfelder[3-6]. The precise form of the expressions depends on the specific definition of the spherical harmonics; in the present context the most useful are the unnormalized forms

$$\Theta_\ell^m(\vartheta,\varphi) = e^{im\varphi} P_\ell^{|m|}(\cos\vartheta) \quad , \quad \Omega_\ell^m(\vartheta,\varphi) = e^{im\varphi} P_\ell^m(\cos\vartheta) \tag{2a}$$

and the normalized form

$$Y_\ell^m(\vartheta,\varphi) = \left[(2\ell+1)(\ell-m)!/4\pi(\ell+m)!\right]^{\frac{1}{2}} e^{im\varphi} P_\ell^m(\cos\vartheta) \, . \tag{2b}$$

Buehler and Hirschfelder[5] consider in detail the case $\vartheta_3 = 0$ and put

$$|Q_1Q_2|^{-1} = \sum B(\ell_1,\ell_2,|m|;r_1,r_2,a)\ \Theta_{\ell_1}^{-m}(\vartheta_1,\varphi_1)\ \Theta_{\ell_2}^{m}(\vartheta_2,\varphi_2)$$
$$\left[\ell_1,\ell_2 = 0,1,\cdots \ ; \ -\ell_< \le m \le \ell_< \ ; \ \ell_< = \min(\ell_1,\ell_2)\right] \, . \tag{3}$$

They have shown that the form of the radial functions B differs according to the relative values of r_1, r_2 and $r_3 = a$; there are, in fact, four distinct regions defined by the following inequalities (see figure 1a):

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[3] B. C. Carlson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc., 46, 215 (1950).

[4] M. E. Rose, J. Maths. and Physics, 37, 215 (1958).

[5] a. R. J. Buehler and J. O. Hirschfelder, Phys. Rev., 83, 628 (1951); b. ibid. 85, 149 (1952).

[6] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids (J. Wiley and Sons, New York, 1954).

$$S_o: |r_1 - r_2| \le r_3 \le r_1 + r_2 \quad ; \qquad S_1: r_1 \ge r_2 + r_3 \quad ,$$
$$S_2: r_2 \ge r_1 + r_3 \quad ; \qquad S_3: r_3 \ge r_1 + r_2 \quad . \tag{4}$$

The same arguments apply to the more general expansions for arbitrary values of the angle ϑ_3 and of the power n of r .

$$r^n = \sum_{\underset{\sim}{\ell},\underset{\sim}{m}} \left[{}_2R(n; \ell_1, \ell_2, \ell_3, m_1, m_2, m_3; r_1, r_2, r_3) \prod_1^3 \Omega_{\ell_s}^{m_s}(\vartheta_s, \varphi_s) \right] \quad ; \tag{5}$$

if either of the definition (2a) or (2c) is used for the spherical harmonics, the corresponding radial functions differ from those in (5) by constants only; the subscripts Θ or Y will be added to ${}_2R$ in such cases.

For the inverse first power, $n = -1$, the functions ${}_2R \equiv {}_2R_i$ vanish in each of the "outer" regions S_i $(i = 1,2,3)$ unless

$$\ell_i = \ell_j + \ell_k \quad ; \quad \ell_s \ge 0 \qquad (s = 1,2,3) \ , \tag{6a}$$

and

$$m_i + m_j + m_k = 0 \quad , \quad |m_s| \le \ell_s \qquad (s = 1,2,3) \quad ; \tag{6b}$$

throughout this paper (i,j,k) denote permutations of $(1,2,3)$. If (6) is satisfied, ${}_2R_i$ consists of a single term

$${}_2R_i = {}_2K_i(-1; \ell_i, \ell_j, \ell_k, m_i, m_j, m_k) r_j^{\ell_j} r_k^{\ell_k} / r_i^{\ell_i + 1} \tag{7}$$

where the coefficients ${}_2K_i$ can be expressed in terms of Wigner coefficients[3,4] or as ratios of factorials[5,6].

For the overlap region S_o , Buehler and Hirschfelder[5,6] found an expression for B_o as a double power series in r_1/a and r_2/a for which they tabulated the coefficients as ratios of integers for $0 \le m \le \ell_1 \le \ell_2 \le 3$. They could not derive a generally valid formula in this region, though in their later paper[5b] they gave a (rather cumbersome) generating function for the function B_o.

The aim of the present paper is to derive generally valid expressions for B_o or ${}_2R_i$ in all the regions; but for the sake of greater symmetry the vector $\underset{\sim}{r} = (r, \vartheta, \varphi)$ in (5) will be understood to mean, not the vector Q_1Q_2, i.e. $\underset{\sim}{r}_2 + \underset{\sim}{r}_3 - \underset{\sim}{r}_1$, but the vector sum $\underset{\sim}{r}_1 + \underset{\sim}{r}_2 + \underset{\sim}{r}_3$; the corresponding radial functions ${}_2R$ differ only by the factor $(-)^{\ell_3}$. As in I and II, the functions are derived as solutions of sets of partial differential equations; they can be expressed in terms of the Appell functions F_4, which form a generalization to two variables of the hypergeometric function (1):

$$F_4(\alpha, \beta; \gamma, \gamma'; \xi, \eta) = \sum \frac{(\alpha)_{u+v}(\beta)_{u+v}}{(\gamma)_u(\gamma')_v\, u!v!}\, \xi^u \eta^v \tag{8}$$

summed over all non-negative values of u and v. The theory of these functions is given in detail in the monographs by Appell and Kampé de Fériet[7,8]; most of the relevant formulas are to be found in Chapter 5 of the Bateman Manuscript Project[9], but for the benefit of the reader, all the formulas utilized in the present paper will be collected in the Appendix. The differential equation do not involve the azimuthal quantum numbers m, and hence the nature of the functions ${}_2R$ does not depend on these numbers; they can only affect the leading coefficients. In the outer regions these constants can be determined from the results of I and II, and in the inner region S_o indirectly, by means of certain linear relations between Appell functions along critical lines. They can be expressed, as in II, by means of 3j-symbols, Wigner coefficients, or integrals of triple products of spherical harmonics (Gaunt's coefficients)[10-11].

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[7] P. Appell, Sur les fonctions hypergéometriques de plusieurs variables, Mémorial des Sciences Mathématiques, Fasc. III (Gauthier-Villars, Paris, 1925).

[8] P. Appell and J. Kampé de Fériet, Fonctions hypergéometriques et hypersphériques, Polynômes d' Hermite (Gauthier-Villars, Paris, 1926).

[9] Bateman Manuscript Project, A. Erdélyi ed., Higher Transcendental Functions, (McGraw Hill, New York, 1953); referenced directly by the prefix B.

[10] See refs. 3-5 and 10 of II.

[11] J. A. Gaunt, Phil. Trans. Roy. Soc. A. 228, 157 (1929).

It is found that for $n = -1$ the functions ${}_2R \equiv {}_2R_o$ appear in the region S_o with non-zero coefficients whenever

$$|\ell_1 - \ell_2| \leq \ell_3 \leq \ell_1 + \ell_2 \quad , \quad \ell_1 + \ell_2 + \ell_3 \;=\; \text{even} \tag{9}$$

so that by confining attention to this case it would not be possible to determine the leading coefficients in this region, unless at least one of the equations (6a) is satisfied. In consequence the general case (5) is considered from the start; the resulting formulas are valid for arbitrary values of n in the outer regions, but in S_o only for integer $n \geq -1$. The formulas obtained for S_1, S_2 and S_3 can be put into an operational form which permit generally valid expansions to be derived in these regions for any function of r; this will be done in section 4. Within S_o, on the other hand, the Laplacean operator applied to the expansion for r^{-1} does not vanish; this gives an analogous expansion for the 3-dimensional Dirac delta function and its derivatives.

2. Mathematical Derivation

The functions r^n satisfy the differential equation

$$\nabla_1^{\,2}(r^n) \;=\; \nabla_2^{\,2}(r^n) \;=\; \nabla_3^{\,2}(r^n) \;=\; n(n+1)r^{n-2} \tag{10}$$

which when substituted into (5) yields

$$\left[\frac{\partial^2}{\partial r_s^{\,2}} + \frac{2}{r_s}\frac{\partial}{\partial r_s} - \frac{\ell_s(\ell_s+1)}{r_s^{\,2}}\right] R(n,\underset{\sim}{\ell},\underset{\sim}{m}) \;=\; \text{invariant} \quad (s = 1,2,3) \tag{11a}$$

$$= \; n(n+1)\ {}_2R(n-2,\underset{\sim}{\ell},\underset{\sim}{m}) \quad . \tag{11b}$$

Furthermore all the ${}_2R$ are homogeneous functions of the variables r_s of degree n, and in the region S_i they are regular as r_j and r_k tend to zero; hence they must be of the form

$$ {}_2R_i = r_j^{\ell_j} r_k^{\ell_k} r_i^{n-\ell_j-\ell_k} G_i(n,\underset{\sim}{\ell},\underset{\sim}{m};r_j/r_i,r_k/r_i) \tag{12} $$

where

$$ G_i(n,\underset{\sim}{\ell},\underset{\sim}{m}) = \sum C_{\mu\nu}(n,\underset{\sim}{\ell},\underset{\sim}{m})(r_j/r_i)^{\mu}(r_k/r_i)^{\nu} \quad . \tag{13} $$

Substitution of (11) into (12) and (13) leads to the recurrence relations

$$ (\mu+2)(2\ell_j+\mu+3)C_{\mu+2,\nu}(n) = (\nu+2)(2\ell_k+\nu+3)C_{\mu,\nu+2}(n) \tag{14a} $$

$$ = (n+1+\ell_i-\ell_j-\ell_k-\mu-\nu)(n-\ell_i-\ell_j-\ell_k-\mu-\nu)C_{\mu\nu}(n) \tag{14b} $$

$$ = n(n+1)C_{\mu\nu}(n-2) \quad . \tag{14c} $$

This defines G_i as an Appell function F_4 in the variables

$$ \xi = r_j^2/r_i^2 \quad , \quad \eta = r_k^2/r_i^2 \quad : \tag{15} $$

$$ G_i(n,\underset{\sim}{\ell},\underset{\sim}{m}) = K_i(n,\underset{\sim}{\ell},\underset{\sim}{m})F_4(\Lambda-\tfrac{1}{2}n,\lambda_i-\tfrac{1}{2}-\tfrac{1}{2}n;\ell_j+\tfrac{3}{2},\ell_k+\tfrac{3}{2};\xi,\eta) \tag{16} $$

where we abbreviate

$$ \Lambda = \tfrac{1}{2}(\ell_1+\ell_2+\ell_3) \quad , \quad \lambda_s = \Lambda-\ell_s \quad (s = 1,2,3) \quad . \tag{17} $$

In view of (11a) and (12), it is easily shown that the function G_i satisfies the set of differential equations of Appell's function (A2) with the variables and parameters defined in (15)-(17). Hence, according to (A3), the complete set of solutions satisfying the differential equations for ${}_2R(n,\underset{\sim}{\ell},\underset{\sim}{m})$ becomes

$$\Psi_{io} = r_i^{\,n}(r_j/r_i)^{-\ell_j-1}(r_k/r_i)^{-\ell_k-1}\,F_4(-\lambda-\tfrac{1}{2}n-\tfrac{3}{2},-\lambda_i-1-\tfrac{1}{2}n;\tfrac{1}{2}-\ell_j,\tfrac{1}{2}-\ell_k;\xi,\eta) \quad , \tag{18a}$$

$$\Psi_{ii} = r_i^{\,n}(r_j/r_i)^{\ell_j}(r_k/r_i)^{\ell_k}\,F_4(\lambda-\tfrac{1}{2}n,\lambda_i-\tfrac{1}{2}n-\tfrac{1}{2};\tfrac{3}{2}+\ell_j,\tfrac{3}{2}+\ell_k;\xi,\eta) \quad , \tag{18b}$$

$$\Psi_{ij} = r_i^{\,n}(r_j/r_i)^{-\ell_j-1}(r_k/r_i)^{\ell_k}\,F_4(\lambda_j-\tfrac{1}{2}n-\tfrac{1}{2},-\lambda_k-1-\tfrac{1}{2}n;\tfrac{1}{2}-\ell_j,\tfrac{3}{2}+\ell_k;\xi,\eta) \quad , \tag{18c}$$

$$\Psi_{ik} = r_i^{\,n}(r_j/r_i)^{\ell_j}(r_k/r_i)^{-\ell_k-1}\,F_4(\lambda_k-\tfrac{1}{2}n-\tfrac{1}{2},-\lambda_j-1-\tfrac{1}{2}n;\tfrac{3}{2}+\ell_j,\tfrac{1}{2}-\ell_k;\xi,\eta) \quad . \tag{18d}$$

Here the first subscript in notation Ψ_{it} indicates which radius r_i occurs in the denominator of the definitions (15) for ξ and η, and the second subscript shows that $\Psi_{it}/r_i^{\,n}$ becomes singular as $r_t \to 0$; if $t = 0$ this ratio becomes singular whichever radius tends to zero. Further we denote the function ${}_2R$ in the region S_w by ${}_2R_w$ as in (12), and K_{wit} the coefficients of (18) in the expression for ${}_2R_w$:

$${}_2R_w(n,\underset{\sim}{\ell},\underset{\sim}{m}) = \sum_t K_{wit}(n,\underset{\sim}{\ell},\underset{\sim}{m})\,\Psi_{it}(n,\underset{\sim}{\ell}) \quad . \tag{19}$$

In view of (A1) the Appell functions in the outer regions are convergent only if $i = w$, and the regularity of ${}_2R_i$ for small values of r_j and r_k requires that the solution is of the form (12),

$$K_{iit} \equiv 0 \quad , \quad t \neq i \quad ; \quad K_{iii} = K_i \quad . \tag{20}$$

In the region S_o the series are always divergent unless they terminate; in those cases in which (18) leads to useful expansions the choice of i is somewhat arbitrary. The nature of the functions Ψ of (19) being known from (18), it remains to calculate the coefficients K_i and K_{oit} .

To determine K_i in S_i we provisionally combine $\underset{\sim}{r}_j + \underset{\sim}{r}_k$ to a vector $(r_{jk}, \vartheta_{jk}, \varphi_{jk})$; then according to (19) of I and the addition theorem for the P (cos ϑ_{12}) (B 3.11.2) we have

$$r^n = \sum_{\underset{\sim}{\ell},\underset{\sim}{m}} \left\{ r_i^{\,n-\ell} r_{jk}^{\,\ell} (-)^{\ell+m} \Omega_\ell^{-m}(\vartheta_i, \varphi_i)\, \Omega_\ell^{m}(\vartheta_{jk}, \varphi_{jk}) \times \right.$$
$$\left. \times \frac{(-\tfrac{1}{2}n)_\ell}{(\tfrac{1}{2})_\ell} F(\ell-\tfrac{1}{2}n, -\tfrac{1}{2}-\tfrac{1}{2}n; \tfrac{3}{2}+\ell; \frac{r_{jk}^2}{r_i^2}) \right\} . \tag{21}$$

This expression involves r_{jk} only through the solid harmonics $r_{jk}^{\ell}\,\Omega_\ell^m$ and through positive even powers $r_{jk}^{2\nu}$; both factors are regular functions of r_j and r_k . If these products, in turn, are expanded in spherical harmonics of (ϑ_j, φ_j) and (ϑ_k, φ_k) , we see from (5) and (32)-(34) of II that the lowest power 2ν which contributes to terms for which $\ell_j + \ell_k - \ell = 2\lambda$ occurs for $\nu = \lambda$, irrespective of n . We have from (5) and (30) of II:

$$r_{jk}^{\ell+2\lambda}\, \Omega_\ell^m(\vartheta_{jk}, \varphi_{jk}) = (-)^m \sum r_j^{\ell_j} r_k^{\ell_k}\, \Omega_{\ell_j}^{m_j}(\vartheta_j, \varphi_j)\, \Omega_{\ell_k}^{m_k}(\vartheta_k, \varphi_k) \times$$
$$\times \frac{(\tfrac{1}{2}; \ell_j+\ell_k+1)\,\lambda!}{(\tfrac{1}{2};\ell_j)(\tfrac{1}{2};\ell_k)}\; I_\Omega \begin{pmatrix} \ell & \ell_j & \ell_k \\ m & -m_j & -m_k \end{pmatrix} + \cdots \tag{22}$$

where I_Ω is Gaunt's coefficient[11]

$$I_\Omega \begin{pmatrix} \ell & \ell' & \ell'' \\ m & m' & m'' \end{pmatrix} = \int_{-1}^{1} P_\ell^{m}(x) P_{\ell'}^{m'}(x) P_{\ell''}^{m''}(x)\,dx \quad . \tag{23}$$

If we put $\ell = \ell_i$, $m = -m_i$, $\lambda = \lambda_i$ and use the abbreviations (17), the constant $K_i(n, ,m)$ in (16) is found from (21)-(23) and (1)

$$K_i(n,\underset{\sim}{\ell},\underset{\sim}{m}) = (-)^{\ell_i} \frac{(\ell_i+\tfrac{1}{2})(-\tfrac{1}{2}n;\Lambda)(-\tfrac{1}{2}-\tfrac{1}{2}n;\lambda_i)}{(\tfrac{1}{2};\ell_j)(\tfrac{1}{2};\ell_k)}\; I_\Omega \begin{pmatrix} \ell_i & \ell_j & \ell_k \\ -m_i & -m_j & -m_k \end{pmatrix} . \tag{24}$$

The radial functions ${}_2R_i$ in the outer regions are thus completely determined by (12), (16) and (24). The corresponding expressions in the overlap region S_o can be obtained by means of the linear relation (A8) between the four solutions (A3) of the differential equations (A2) on the critical lines (A4) (see figure 1). These lines correspond exactly to the boundaries L_i separating the regions S_i from S_o, but the ${}_2R_w$ must be brought to a common set of variables before (A8) can be applied. In (18) we can transform ψ_{jj}, on which ${}_2R_j$ solely depends, into a linear combination of ψ_{ii} and ψ_{ij} by means of (A6), but the resulting series are in general divergent. The only cases in which (A6) leads to an expression which can be usefully interpreted without recourse to contour integration, are those in which the initial series terminates, i.e. where α or β is a non-positive integer; then (A6) shows that one of the series in the new variables has zero coefficient and the other terminates. Applying this argument to the set (18) we find we can deal with two cases:

(A) n is a non-negative even integer; then r^n is analytic throughout and can be represented by a finite expansion common to all regions; the value of i in (18) and (19) is immaterial, and the result can be expressed in a form involving only positive powers of the r_s.

(B) n is an odd integer ≥ -1; then

$$\psi_{jj} = T_{ji}\,\psi_{ij} \quad ; \quad T_{ji} = (-)^{\frac{1}{2}+\frac{1}{2}n-\lambda_j}\,\frac{\Gamma(\frac{3}{2}+\ell_i)\,\Gamma(\frac{1}{2}+\ell_j)}{\Gamma(\Lambda-\frac{1}{2}n)\,\Gamma(2+\frac{1}{2}n+\lambda_k)} \quad . \tag{25}$$

Now since ${}_2R_o = {}_2R_s$ on $L_s (s = 1,2,3)$, the coefficients K_{oit} in (19) can be determined from (24) and (A8) leading to

$$K_{oii} = \tfrac{1}{2}K_i \;,\quad K_{oij} = \tfrac{1}{2}K_{jij} = \tfrac{1}{2}K_j/T_{ji} \;,\quad K_{oik} = \tfrac{1}{2}K_{kik} = \tfrac{1}{2}K_k/T_{ki} \tag{26}$$

$$K_{oio} = -\tfrac{1}{2}K_i' \,\frac{\Gamma(\frac{3}{2}+\ell_j)\,\Gamma(\frac{3}{2}+\ell_k)\,\Gamma(1+\frac{1}{2}n-\Lambda)\,\Gamma(\frac{3}{2}+\frac{1}{2}n-\lambda_i)}{\Gamma(\frac{1}{2}-\ell_j)\,\Gamma(\frac{1}{2}-\ell_k)\,\Gamma(2+\frac{1}{2}n+\lambda_i)\,\Gamma(\frac{5}{2}+\frac{1}{2}n+\Lambda)} \tag{27a}$$

$$= (-)^{\ell_i+1}\,\tfrac{1}{2}(\ell_i+\tfrac{1}{2})\,\frac{(\frac{1}{2};\ell_j+1)\,(\frac{1}{2};\ell_k+1)}{(1+\frac{1}{2}n;\lambda_i+1)\,(\frac{3}{2}+\frac{n}{2};\Lambda+1)}\, I_{\Omega}\begin{pmatrix}\ell_i & \ell_j & \ell_k\\ -m_i & -m_j & -m_k\end{pmatrix}. \tag{27b}$$

The expression (27a) is meaningless $(0.\infty)$ if $\lambda_i > \frac{1}{2}+\frac{1}{2}n$; nevertheless (27b) is valid for all values of $\underset{\sim}{\ell}$ and $\underset{\sim}{m}$ satisfying (6b) and (9); the result could first be derived for n raised by a sufficiently large even number for this difficulty to disappear and then be extended by repeated application of (11b).

3. Discussion of Results

As in II, it is convenient to factorize the expression for the functions ${}_2R$ in (5) in the form

$$ {}_2R(n,\underset{\sim}{\ell},\underset{\sim}{m};r_1,r_2,r_3) = {}_2K'(\underset{\sim}{\ell},\underset{\sim}{m})\ {}_2R'(n,\underset{\sim}{\ell};r_1,r_2,r_3) \tag{28} $$

where the constant ${}_2K'$ is independent of n and the values of r_s and comprises the complete dependence on $\underset{\sim}{m}$. The selection preferred by the writer is

$$ {}_2K'(\underset{\sim}{\ell},\underset{\sim}{m}) = (\ell_1+\tfrac{1}{2})(\ell_2+\tfrac{1}{2})(\ell_3+\tfrac{1}{2})\ I_{\Omega}\begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} \tag{29} $$

where the I_{Ω} are Gaunt's coefficients[11] defined in (23), or if the un-normalized 3j-symbols defined in (26) and (29) of II and the abbreviations (17) are used

$$ {}_2K'(\underset{\sim}{\ell},\underset{\sim}{m}) = 2(-)^{\Lambda}\ \frac{\Lambda!}{(2\Lambda+1)!}\ \prod_{s=1}^{3}\left[\frac{(\ell_s-m_s)!}{\lambda_s!}\ (\ell_s+\tfrac{1}{2})\right]\ U\begin{pmatrix} \ell_1 & \ell_2 & \ell_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} . \tag{30} $$

The second factor ${}_2R'$ in (28) differs according to the region S_w ; in the "outer" regions S_i we obtain from (12), (16), (17) and (24)

$$ {}_2R_i'(n,\underset{\sim}{\ell};r_i,r_j,r_k) = (-)^{\ell_i}\ \frac{(-\frac{1}{2}n;\Lambda)(-\frac{1}{2}-\frac{1}{2}n;\lambda_i)}{(\frac{1}{2};\ell_j+1)(\frac{1}{2};\ell_k+1)} \left(\frac{r_j}{r_i}\right)^{\ell_j}\left(\frac{r_k}{r_i}\right)^{\ell_k} r_i^{\,n} $$
$$ F_4(\Lambda-\tfrac{1}{2}n,\ \lambda_i-\tfrac{1}{2}-\tfrac{1}{2}n;\ \ell_j+\tfrac{3}{2},\ \ell_k+\tfrac{3}{2};\ r_j^2/r_i^2,\ r_k^2/r_i^2) \quad . \tag{31} $$

In the overlap region S_o , the expressions for ${}_2R'$ are valid, according to the discussion of the previous chapter, only if n is an integer

≥ 1 ; two cases are to be distinguished

(A) n even ≥ 0 ; then $_2R$ is the same expression in all four regions

$$_2R'_1 = {_2R'_2} = {_2R'_3} = {_2R'_0} \tag{32}$$

(B) n odd ≥ -1 ; then according to (18), (19), (26), and (27)

$$_2R'_0 = \tfrac{1}{2}({_2R'_1} + {_2R'_2} + {_2R'_3}) - \tfrac{1}{2}(-)^{\ell_i} \frac{(\frac{1}{2};\ell_j)(\frac{1}{2};\ell_k)}{(1+\frac{1}{2}n;\lambda_i+1)(\frac{5}{2}+\frac{1}{2}n;\lambda+1)} \times r_i^n \left(\frac{r_j}{r_i}\right)^{\ell_j}\left(\frac{r_k}{r_i}\right)^{\ell_k} F_4\left(-\frac{3}{2}-\tfrac{1}{2}n-\lambda, -1-\tfrac{1}{2}n-\lambda_i; \tfrac{1}{2}-\ell_j, \tfrac{1}{2}-\ell_k; \frac{r_j^2}{r_i^2}, \frac{r_k^2}{r_i^2}\right) . \tag{33}$$

Equations (31) and (33) show that for odd n those functions which represent $_2R'$ in the outer regions appear with half their coefficient in the overlap region and vanish in the other outer regions; the last term in (33), which is specific to $S_{o\kappa}$, could equally well be expressed in terms of Appell functions with r_j or r_k in the denominator of the arguments, the results being a polynomial in each case.

If the spherical harmonics in (5) are given in their normalized form (2c), the corresponding radial functions $_2R_\lambda$ factorize, in analogy to (28) into functions $_2R'$, which are the same as in (31) and (33), and constants $_2K'_\lambda$ given, in view of (2) and (29), (30)

$$_2K'_\lambda = (-)^{m_2} 4\pi^2 (\ell_1,-m_1|Y_{\ell_2}|\ell_3,m_3) \tag{34a}$$

$$= (-)^{m_2}(4\pi)^{3/2}\left[(2\ell_1+1)(2\ell_2+1)(2\ell_3+1)\right]^{\frac{1}{2}}\begin{pmatrix}\ell_1 & \ell_2 & \ell_3\\ m_1 & m_2 & m_3\end{pmatrix}\begin{pmatrix}\ell_1 & \ell_2 & \ell_3\\ 0 & 0 & 0\end{pmatrix} \tag{34b}$$

in terms of integrals of products of three harmonics over the unit sphere or of (normalized) 3j-symbols (cf. (37), (38) and ref. 6 of II).

The main application of the expressions derived in this paper is likely to be the evaluation of integrals for the interaction between two "charge" distributions referred to different origins and interacting with a negative power of the distance

$$\iint \rho_1(r_1)\, \rho_2(r_2) |Q_1Q_2|^n \, d^3\underset{\sim}{r}_1 \, d^3\underset{\sim}{r}_2 \quad . \tag{35}$$

If the functions ρ are expanded in spherical harmonics

$$\rho_\mu = \sum w_\mu(\ell_\mu, m_\mu, r_\mu) \;\Omega_{\ell_\mu}^{m_\mu}(\vartheta_\mu, \varphi_\mu) \quad , \quad \mu = 1,2 \tag{36}$$

the expansion for $|Q_1Q_2|^n$ is given by (5) and (28)-(34), except for a factor $(-)^{\ell_1}$ in each term as discussed in the introduction and by Carlson and Rushbrooke[3]. The orthogonality of the functions leads to straightforward integrations over the angles for common values of ℓ_1 , m_1 , ℓ_2 , m_2 , and the results have to be summed over all compatible values of ℓ_3 . The spherical harmonics of ϑ_3 and φ_3 are best left unnormalized, even if the expansion (36) is given in normalized harmonics; in particular for the case considered by Buehler and Hirschfelder[5], $\vartheta_3 = 0$, we have $\Omega = 1$ $(m_3 = 0)$, $\Omega = 0$ $(m_3 \neq 0)$.

For $n = -1$ the results in the outer regions have been known from previous work[3-6]; for other negative integer values of n and $\vartheta_3 = 0$ an expansion has been derived by Prigogine[12] by means of the appropriate Gegenbauer polynomials[1], which were then re-expanded in terms of spherical harmonics; the resulting expressions are valid in the region S_3 only, though this limitation has not been noticed by Prigogine. The complete analysis of the expansions for general values of n and $\vartheta_3 = 0$, which implies a summation over ℓ_3 in (5), leads to expressions for the radial factors which involve more complicated functions than the Appell polynomials used in the present paper, and for this reason will not be discussed here.

The most important case considered is $n = -1$, for which we obtain for ${}_2R'$ in (31) and (33) .

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[12] I. Prigogine, The Molecular Theory of Solutions (North-Holland Publishing Co., Amsterdam, 1957).

$$_2R_i' = (-)^{\ell_i} \frac{4(2\ell_i-1)!!}{(2\ell_j+1)!!(2\ell_k+1)!!} \frac{r_j^{\ell_j} r_k^{\ell_k}}{r_i^{\ell_i+1}} \delta_{\ell_i,\ell_j+\ell_k} \tag{37}$$

in agreement with previous work[3-6], and for the overlap region S_o

$$_2R_o' = \tfrac{1}{2}({}_2R_1' + {}_2R_2' + {}_2R_3') - (-)^{\ell_3} \frac{(2\ell_1-1)!!(2\ell_2-1)!!}{(2\lambda_3+1)!!2^{\Lambda}(\Lambda+1)!} \left(\frac{a}{r_1}\right)^{\ell_1+1} \left(\frac{a}{r_2}\right)^{\ell_2+1} a^{-1}$$
$$\times\ F_4(-1-\Lambda, -\tfrac{1}{2}-\lambda_3; \tfrac{1}{2}-\ell_1, \tfrac{1}{2}-\ell_2; r_1^2/a^2, r_2^2/a^2) \tag{38}$$

where $(2k)!! = 2^k\, k!$, $(2k-1)!! = 2^k\, (\tfrac{1}{2})_k$ (cf. (43) of I); the function F_4 in (38) represents a polynomial of degree $\Lambda + 1$ in ξ and η , or $2(\Lambda+1)$ in (r_1/a) and (r_2/a) . By substituting (29), (30) and (38) into (5) with the special value $\theta_3 = 0$, using the harmonics Θ of (2) instead of Ω , and summing over ℓ_3 the writer has been able to reproduce and extend the list of coefficients tabulated by Buehler and Hirschfelder[5,6].

The lack of an expansion for $n < -1$ valid within S_o is a serious limitation to the applicability of the method to molecular problems; it precludes its use for the evaluation of relativistic corrections to Coulomb energies, for which $n = -2$, or of van der Waals energies $(n = -6)$ for interpenetrating or even closely approaching elongated distributions. The existence of expansions valid in S_o for fractional n appears doubtful because of the highly complicated branch points of the function $_2R_o'$ corresponding to the physical singularity at $r = 0$. On the other hand if the relation

$$\nabla^2(r^{-1}) = -4\pi\, \delta^3(r) , \tag{39}$$

where δ^3 is the three-dimensional Dirac delta function, is applied to (37) and (38), an expansion for δ^3 is obtained, analogous to (5) and (28)-(33) with

$$ {}_2R_i'(\delta,\underset{\sim}{\ell}) = 0 \quad , \quad i = 1,2,3 \tag{40a} $$

$$ {}_2R_o'(\delta,\ell) = \frac{(-)^{\ell_3+1}\,(2\ell_1-1)!!(2\ell_2-1)!!}{\pi(2\lambda_3-1)!!2^{\Lambda-2}\Lambda!} \left(\frac{a}{r_1}\right)^{\ell_1+1} \left(\frac{a}{r_2}\right)^{\ell_2+1} a^{-3} \times $$
$$ \times F_4(-\Lambda,\tfrac{1}{2}-\lambda_3;\tfrac{1}{2}-\ell_1,\tfrac{1}{2}-\ell_2;r_1{}^2/a^2,r_2{}^2/a^2) \quad . \tag{40b} $$

In contrast ot (31) and (33), the functions ${}_2R'(\delta)$ are discontinuous along the boundaries L_s ; hence, although the Laplacean operator could, in turn, be applied to δ^3 , any integral making use of such an expansion for $\nabla^2(\delta^3)$ would have to be supplemented by line integrals taken along the L_i , and correspondingly for higher derivatives.

Even in such cases, where the complete expansion is known in S_o , its use for the numerical evaluation of integrals may give rise to considerable difficulties. The joint degree in r_1 and r_2 of the terms in ${}_2R_o'$

$$ w = -2 - \ell_1 - \ell_2 + \mu + \nu \tag{41} $$

may be positive as well as negative; on the other hand for large values of (r_1+r_2) the functions cannot increase faster than with this sum raised to the n-th power. Hence for $n = -1$ all those terms in a given ${}_2R_o'$ with a constant value of $w \geq 0$ must contain the factor $(r_1-r_2)^{w+1}$, which in view of (4) remains bounded. If, therefore, an attempt is made to evaluate the integrals in (35) and (36) term by term over the expansions for $1/r$ in (12) and (13), we obtain repeated integrals of the form

$$ a^{\ell_1+\ell_2+1-\mu-\nu}\, C_{\mu\nu} \int r_1{}^{1-\ell_1+\mu}\, W_1(\ell_1,m_1;r_1)dr_1 \times $$
$$ \times \int r_2{}^{1-\ell_2+\nu}\, W_2(\ell_2,m_2;r_2)dr_2 \tag{42} $$

with limits corresponding to the boundaries of S_o . These terms are likely to be largest for large μ and ν , but will add up to a small sum when summed over constant values of w , thereby reducing the accuracy of any numerical method employed. To avoid this difficulty we could first calculate ${}_2R_o'(-1,\underset{\sim}{\ell})$ over a grid in S_o and evaluate the integrals by a suitable two-dimensional quadrature formula. This is bound to be more cumbersome than the repeated integration in (42) and also necessitates knowledge of recurrence formulas by which R_o can be computed for large $\underset{\sim}{\ell}$ from values with small $\underset{\sim}{\ell}$ without loss of accuracy; the writer has been unable to derive such recurrence formulas, not only those involving 3 functions as suggested by Appell[7,8]; but even numerically useful formulas involving 4 or more terms.

The usefulness of the two-center expansion for molecular integrals would thus appear limited to the following special cases:

(a) The expansion for ρ_1 and ρ_2 only extend to small values of ℓ, i.e. the change distributions are atomic (Coulomb integrals). For this case other methods are available, but the present approach seems to be competitive in simplicity and efficiency.

(b) Compared with the distance $r_3 = a$, ρ_1 and ρ_2 are sufficiently concentrated so that the integrand becomes negligible outside the region S_3 . In this case the two-centre expansion is the most convenient method for the evaluation of the integrals; its usefulness could be increased considerably by numerical methods for the approximate evaluation of small, but not negligible contributions from the region S_o .

(c) The functions ρ_1 and ρ_2 are of such a nature that the integrals over S_o of their products with the ${}_2R_o'$ can be evaluated analytically; this approach again necessitates the extablishment of recurrence relations, in this case for the integrals. For exponential functions ρ this method will be treated in a separate paper.

In a recent paper Fontana[13] has sketched a two-center expansion analogous to (27a) of I, which is independent of the region S_i , but

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[13] P. R. Fontana, J. Mathematical Physics, 2, 825 (1961).

introduces powers of $(r_1^2+r_2^2+r_3^2)$ in the denominator. The explicit formulas are not given by Fontana, and for the reasons discussed at the end of Section 3 of II the writer considers that the expansion will involve functions of greater complexity than those considered in the present series of papers.

More recently, Chiu[14] has derived some of the results of this paper by means of irreducible tensor algebra. Chiu also considers cases for which the functions depend on the angles of $\underset{\sim}{r}_2 + \underset{\sim}{r}_3 - \underset{\sim}{r}_1$ provided $\vartheta_3 = 0$; a complete analysis of such cases would require the use of 6j-symbols and has been purposely postponed by the writer.

4. An Expansion Theorem for Arbitrary Functions f(r)

As in I and II, the formula (31) for the functions ${}_2R_i'$ in the outer regions, though not (33) for ${}_2R_o'$, can be put in an operational form. For the factor in the general term of (31) and (8) which depends on n we obtain

$$(-\tfrac{1}{2}n;\, \Lambda+u+v)(-\tfrac{1}{2}-\tfrac{1}{2}n;\, \lambda_i+u+v)\, r_i^{\,n-\ell_j-\ell_k-2u-2v} = \tag{43}$$
$$= \frac{(-r_i)^{\ell_i}}{2^{\ell_j+\ell_k+2u+2v}} \left(\frac{1}{r_i}\frac{\partial}{\partial r_i}\right)^{\ell_i} \frac{1}{r_i}\left(\frac{\partial}{\partial r_i}\right)^{2\lambda_i+2u+2v} r_i^{\,n+1} .$$

Hence if we expand any function $f(r)$ which can be represented as a power series in r, we obtain in S_i in analogy to (5), (28) and (29)

$$f(r) = \sum \left[{}_2f' \cdot {}_2K'(\underset{\sim}{\ell},\underset{\sim}{m}) \cdot \prod \Omega_{\ell_s}^{m_s}(\vartheta_s, \varphi_s) \right] \tag{44}$$

where

$${}_2f_i'(\underset{\sim}{\ell};r_s) = \sum_{u,v} \frac{4\, r_i^{\ell_i}\, r_j^{\ell_j+2u}\, r_k^{\ell_k+2v}}{(2u)!!(2v)!!(2\ell_j+2u+1)!!(2\ell_k+2v+1)!!} \times$$
$$\left(\frac{1}{r_i}\frac{\partial}{\partial r_i}\right)^{\ell_i} \frac{1}{r_i}\left(\frac{\partial}{\partial r_i}\right)^{\ell_j+\ell_k-\ell_i+2u+2v} \left[r_i f(r_i)\right] , \tag{45}$$

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[14] Y. N. Chiu, To be published.

or using modified spherical Bessel functions $i_\ell(x)$

$$ {}_2f_i' = 4r_i^{\ell_i}\left(\frac{1}{r_i}\frac{\partial}{\partial r_i}\right)^{\ell_i}\frac{1}{r_i}\;\frac{i_{\ell_j}(r_j\partial/\partial r_i)\,i_{\ell_k}(r_k\partial/\partial r_i)}{(\partial/\partial r_i)^{\ell_i}}\left[r_i f(r_i)\right] \quad . \tag{46}$$

As in I and II, this expression factorizes if $f(r)$ is a spherical Bessel function

$$ f(r) = w_o(Kr) \quad , \quad w = j, y, h^{(1)}, h^{(2)} \quad ; \tag{47}$$

then in view of (56)-(60) of I

$$ {}_2f_i' = (-)^{\Lambda}\, j_{\ell_j}(Kr_j)\; j_{\ell_k}(Kr_k)\; w_{\ell_i}(Kr_i) \quad , \tag{48}$$

and for the modified Bessel function $f(r) = i_o(Kr)$

$$ {}_2f_i' = \prod_{s=1}^{3} i_{\ell_s}(Kr_s) \quad , \tag{49a}$$

and for the modified Bessel function of the second kind $f(r) = k_o(Kr)$

$$ {}_2f_i' = (-)^{\ell_i}\, i_{\ell_j}(Kr_j)\; i_{\ell_k}(Kr_k)\; k_{\ell_i}(Kr_i) \quad . \tag{49b}$$

For j_o and i_o, which are even functions of the argument, the expansion is invariant on permuting (i,j,k) and is therefore also valid in S_o; for the other Bessel functions, the writer has been unable to find the expression appropriate to S_o.

Acknowledgements

The writer wishes to thank Prof. J. O. Hirschfelder, Dr. M. J. M. Bernal and Dr. Y. N. Chiu for stimulating discussions and advice.

<u>Appendix</u>: Properties of the Appell Functions F_4 .

Appell's function F_4 as defined in (8) represents a polynomial in ξ and η of degree $|\alpha|$ or $|\beta|$ if α or β is a non-positive integer. In all other case F_4 is an infinite series which converges for values ξ and η such that

$$|\xi|^{\frac{1}{2}} + |\eta|^{\frac{1}{2}} < 1 \quad ; \tag{A1}$$

for other values of the variables the function can be defined in terms of contour integrals (cf. (B 5.7.44) and (B 5.8.9,13)). They satisfy the pair of differential equations (B 5.9.12)

$$\xi^2 \frac{\partial^2 z}{\partial \xi^2} + 2\xi\eta \frac{\partial^2 z}{\partial \xi \partial \eta} + \eta^2 \frac{\partial^2 z}{\partial \eta^2} + (\alpha+\beta+1)\left(\xi \frac{\partial z}{\partial \xi} + \eta \frac{\partial z}{\partial \eta}\right) + \alpha\beta z = \tag{A2}$$
$$= \xi \frac{\partial^2 z}{\partial \xi^2} + \gamma \frac{\partial z}{\partial \xi} = \eta \frac{\partial^2 z}{\partial \eta^2} + \gamma' \frac{\partial z}{\partial \eta} \quad .$$

This set has, in general, four linearly independent solutions (p 52 of [8]),

$$\begin{aligned}
z_o &= \xi^{1-\gamma}\eta^{1-\gamma'} F_4(\alpha+2-\gamma-\gamma', \beta+2-\gamma-\gamma'; 2-\gamma, 2-\gamma'; \xi, \eta) \quad , \\
z_i &= F_4(\alpha, \beta; \gamma, \gamma'; \xi, \eta) \quad , \\
z_j &= \xi^{1-\gamma} F_4(\alpha+1-\gamma, \beta+1-\gamma; 2-\gamma, \gamma'; \xi, \eta) \quad , \\
z_k &= \eta^{1-\gamma'} F_4(\alpha+1-\gamma', \beta+1-\gamma'; \gamma, 2-\gamma'; \xi, \eta) \quad ;
\end{aligned} \tag{A3}$$

but the four independent solutions of systems such as (A3) become linearly dependent with constant coefficients on certain critical lines (12 of [8]). For any function F_4 there exist at least three critical lines[15]

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[15] P. Appell, J. des Math. Pures et Appl. , 3rd series, <u>10</u>, 407 (1884).

$$L_i: \sqrt{\xi} + \sqrt{\eta} = 1 \quad ; \quad L_j: \sqrt{\xi} - \sqrt{\eta} = 1 \quad ; \quad L_k: \sqrt{\eta} - \sqrt{\xi} = 1 \tag{A4}$$

which form sections of a single parabola

$$\xi^2 - 2\,\xi\eta + \eta^2 - 2\xi - 2\eta + 1 = 0 \tag{A5}$$

For variations of ξ and η along L_i, Appell has shown that $Z = Z\left[\xi, \eta(\xi)\right]$ taken as a function of ξ satisfies a third-order ordinary differential equation, instead of a fourth-order one as along an arbitrary line; hence (A2) has only three linearly independent solutions on L_i. For the other lines, this dependence follows from the transformation (B 6.11.9)

$$\begin{aligned} F_4(\alpha,\beta;\gamma,\gamma';\xi,\eta) &= \\ \frac{\Gamma(\gamma')\,\Gamma(\beta-\alpha)}{\Gamma(\gamma'-\alpha)\,\Gamma(\beta)}&(-\eta)^{-\alpha}\,F_4(\alpha,\alpha+1-\gamma';\gamma,\alpha+1-\beta;\frac{\xi}{\eta},\frac{1}{\eta}) \\ +\frac{\Gamma(\gamma')\,\Gamma(\alpha-\beta)}{\Gamma(\gamma'-\beta)\,\Gamma(\alpha)}&(-\eta)^{-\beta}\,F_4(\beta,\beta+1-\gamma';\gamma,\beta+1-\alpha;\frac{\xi}{\eta},\frac{1}{\eta}) \end{aligned} \tag{A6}$$

and a corresponding transformation to $(1/\xi, \eta/\xi)$. Appell has not explicitly stated the coefficients relating the functions (A3); the writer has been able to deduce them for restricted values of the parameters only. Considering their behaviour near (1,0) and (0,1), we see that two of the functions are singular in the vanishing variable and two analytic (for fractional values of γ and γ'); regarded as functions of the other variable they are essentially hypergeometric series and since (B 2.1.14)

$$F(\alpha,\beta;\gamma;1) = \Gamma(\gamma)\,\Gamma(\gamma-\alpha-\beta)\left[\Gamma(\gamma-\alpha)\,\Gamma(\gamma-\beta)\right]^{-1}, \tag{A7}$$

$$\mathrm{Re}(\gamma) > \mathrm{Re}(\alpha+\beta),$$

the only relation with constant coefficients which can hold on the line L_s of (4) is

$$\frac{\Gamma(\gamma)\,\Gamma(\gamma')}{\Gamma(\gamma+\gamma'-\alpha-1)\,\Gamma(\gamma+\gamma'-\beta-1)}\, z_o + \varepsilon_{si}\,\frac{\Gamma(2-\gamma)\,\Gamma(2-\gamma')}{\Gamma(1-\alpha)\,\Gamma(1-\beta)}\, z_i +$$

$$+\, \varepsilon_{sj}\,\frac{\Gamma(\gamma)\,\Gamma(2-\gamma')}{\Gamma(\gamma-\alpha)\,\Gamma(\gamma-\beta)}\, z_j + \varepsilon_{sk}\,\frac{\Gamma(2-\gamma)\,\Gamma(\gamma')}{\Gamma(\gamma'-\alpha)\,\Gamma(\gamma'-\beta)}\, z_k \doteq 0 \tag{A8}$$

where

$$\varepsilon_{ss} = 1 \;;\quad \varepsilon_{st} = -1 \;,\quad s \neq t \;. \tag{A9}$$

The precise form of (A8) for the lines L_j and L_k follows from that for L_i and (A6). On the other hand, a more careful investigation of the behaviour of $F(\alpha,\beta;\gamma;x)$ near $x = 1$ (B 2.10.1) shows that (A8) is correct only if all the series terminate which appear with non-vanishing coefficients; otherwise terms of the form $(1-\xi)^{\gamma-\alpha-\beta}$ enter into (A8) which do not add up to zero.

Appell has also stated (p. 19 of [8]) that any three contiguous functions F_4 satisfy a linear recurrence relation, a total of 28 equations if only one parameter at a time changes by unity; but the writer has been unable to find the complete set of such relations in the literature or to derive it, and he doubts the validity of Appell's statement[16].

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[16] Prof. Erdélyi (private communication) has concurred with this opinion.

<u>Text to Figures</u>

Figure 1 The four regions S_w and their boundaries

<u>a</u> as functions of r_1 and r_2 ,

<u>b</u> as functions of ξ and η .

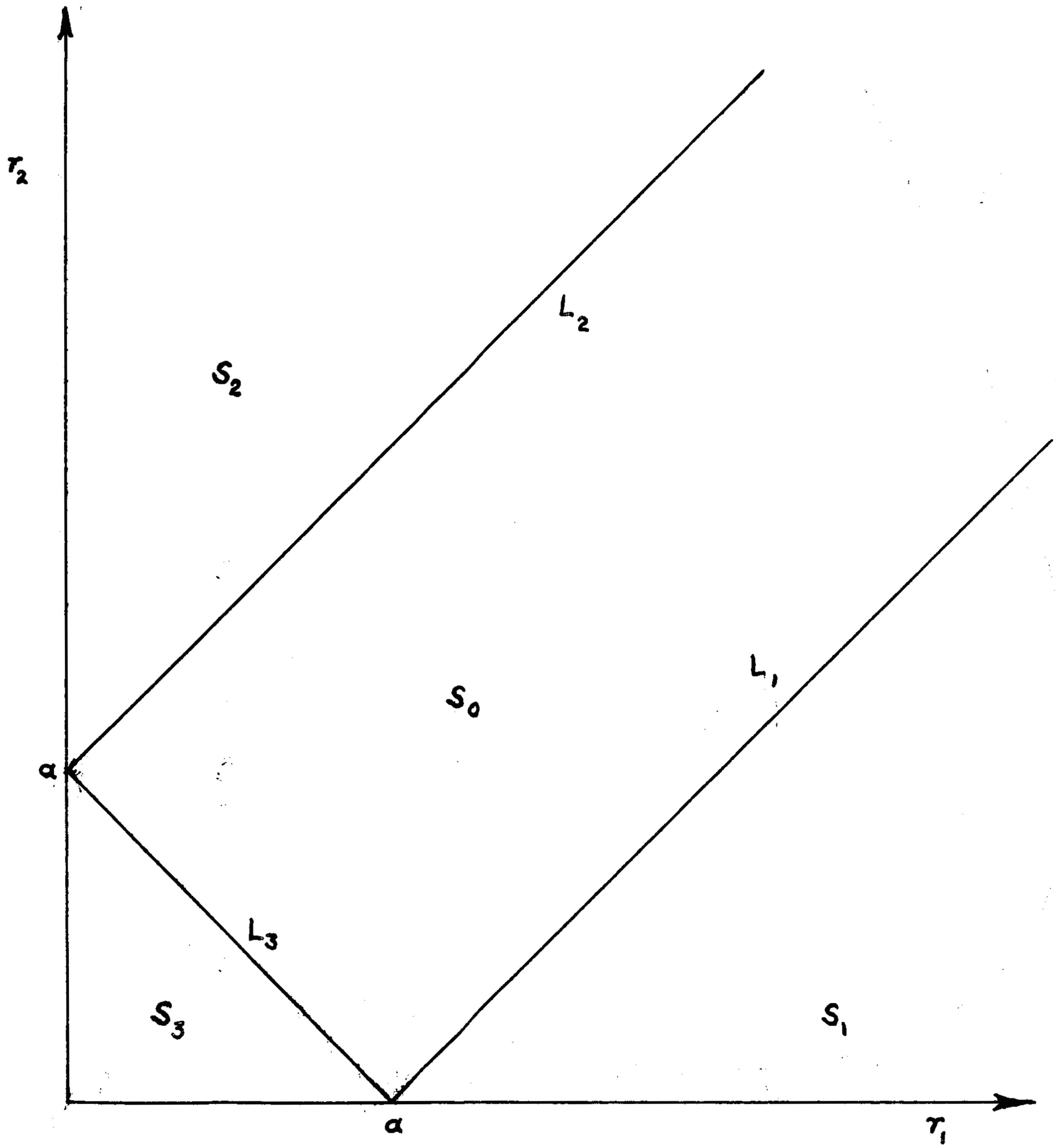

Figure 1a

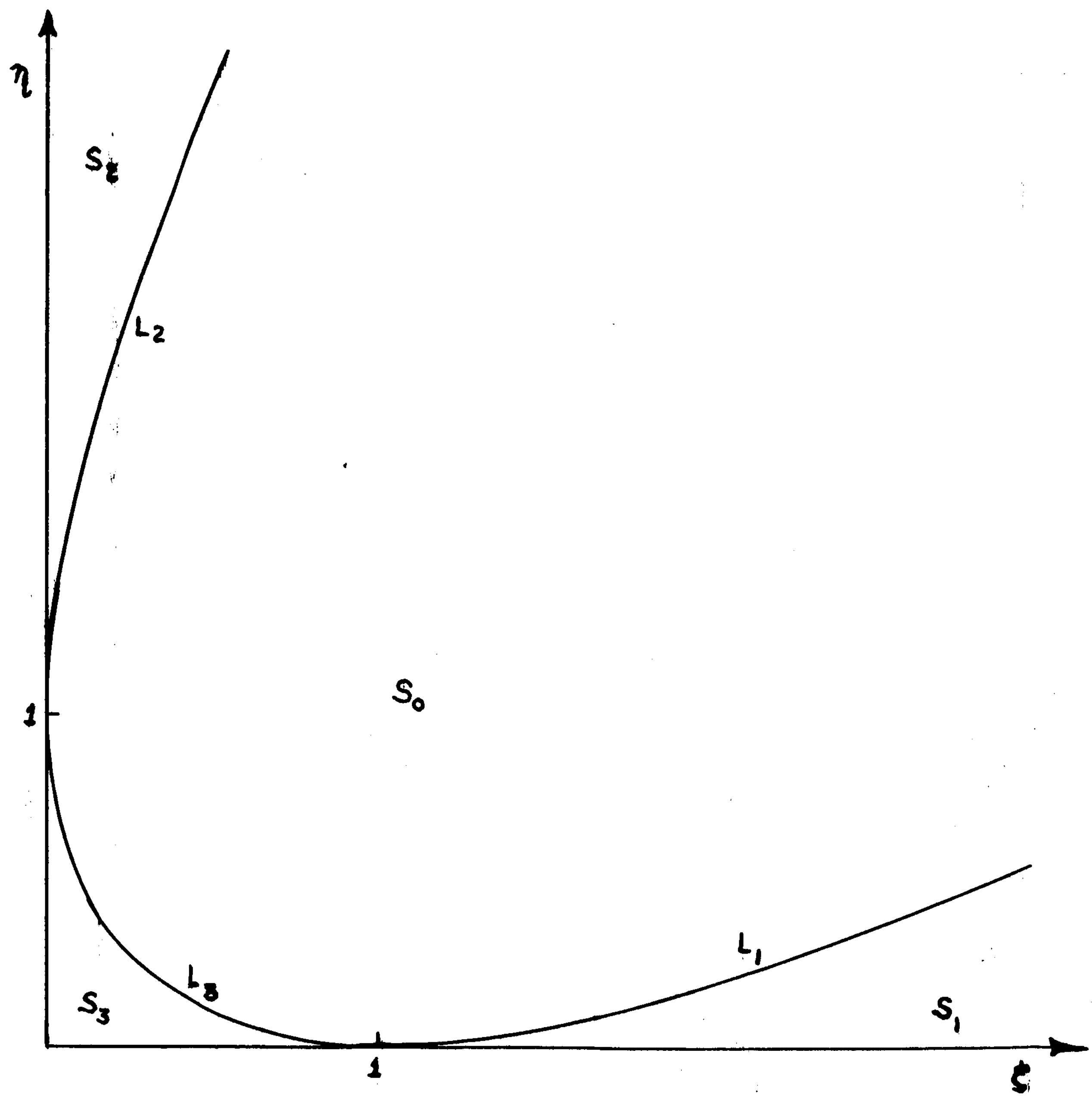

Figure 1b